JP 8-88007

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the electrode for polymer electrolyte fuel cells, and the polymer electrolyte fuel cell using it especially about the electrode of the fuel cell which uses air and oxygen as an oxidizer, using reducing agents, such as pure hydrogen or a methanol, and reforming hydrogen from a fossil fuel, as a fuel.
[0002]
[Description of the Prior Art] A polymer electrolyte fuel cell operates in ordinary temperature, and two or more 1 A/cm high power is obtained by ordinary pressure. In order to enable the output in such high current density, increase of the touch area of the catalyst particle and solid-state polyelectrolyte in an electrode catalyst bed, i.e., reaction area, and improvement in the gas supply ability to a reaction site become important. Among these, in order to raise gas supply ability, the attempt which adds to an electrode catalyst bed by making fluororesins, such as polytetrafluoroethylene (PTFE) resin, into a repellent, and forms the supply way (gas channel) of reactant gas has been made.
[0003] For example, the electrode was produced using the mixed liquor of the carbon powder and the colloidal dispersion liquid of PTFE which supported the catalyst with JP,4-264367,A, and the solid-state polyelectrolyte solution is applied to a catalyst bed front face. Moreover, in JP,5-36418,A, a catalyst and PTFE powder are distributed and kneaded at a solid-state polyelectrolyte solution, and the catalyst bed is produced.
[0004] Furthermore, by 195 pages of J.Electroanal.Chem.197 (1986), the carbon powder given a water-repellent finish by PTFE and the carbon powder which supported the catalyst are mixed, the catalyst bed of a gas diffusion electrode is produced, and the thing using aqueous acids as the electrolytic solution is shown.
[0005] The attempt which raises gas supply ability is carried out by decreasing the thickness of a catalyst bed, without on the other hand the oxygen penetrability of the solid-state polyelectrolyte of a fluorine system adding a fluororesin paying attention to a high thing.
[0006] for example, on U.S. Pat. No. 5,211,984 number specifications A solid-state polyelectrolyte, a catalyst, and the ink-like dispersion liquid of carbon powder are produced by using a glycerol or a tetrabutylammonium salt as a solvent. How to imprint on a solid-state polyelectrolyte film front face, after casting on the film made from PTFE, Or after permuting the solid-state polyelectrolyte film by Na mold, the above-mentioned ink-like dispersion liquid are applied to the front face of the film, stoving is carried out above 125 degrees C, and the method of permuting the solid-state polyelectrolyte film by H mold again is reported. At this time, the thickness of a catalyst bed is as small as less than about 10 micrometers, and supply of reactant gas is performed by diffusing the inside of a solid-state polyelectrolyte.
[0007]
[Problem(s) to be Solved by the Invention] However, by the conventional approach indicated by the above-mentioned patent, the catalyst particle was covered with the fluororesin too much, reaction area decreased, and it had the fault that a polarization property fell. When the carbon powder given a water-repellent finish by PTFE like 195 pages of above-mentioned

J.Electroanal.Chem.197 (1986) on the other hand was used, covering of the catalyst particle by PTFE could be controlled, but since aqueous acids were used as the electrolytic solution, examination of the effectiveness by the existence of addition of the carbon powder given a water-repellent finish when a solid-state polyelectrolyte was added to a catalyst bed, or its appending rate was not performed.

[0008] Moreover, in the above-mentioned United States patent, since a catalyst bed was a precise film which consists only of catalyst support carbon powder and a solid-state polyelectrolyte of a hydrophilic property, it had the fault of a gas channel not having been formed, but the cell voltage in high current density having become low by the flooding by generation water, or becoming unstable.

[0009] This invention solves the above-mentioned conventional technical problem, and it forms in an electrode catalyst bed the gas channel which can make a gas supply condition good, without covering a catalyst particle with a fluororesin too much in the electrode of a polymer electrolyte fuel cell.

[0010]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, the electrode for polymer electrolyte fuel cells of this invention is an electrode which formed in one side of a gaseous diffusion layer the catalyst bed which consists of a solid-state polyelectrolyte and carbon powder which supported the precious metal catalyst at least. The diameter of a primary particle is [the specific surface area of said carbon powder] 700-1000m2/g in 200-350A, the catalyst bed of said electrode has pore as a gas channel, and the diameter of the pore is 0.04-1.0 micrometers. And it is characterized by the structure where the volume of pore is 0.035-0.05cm3/g.

[0011] Furthermore, it is the electrode which formed in one side of a gaseous diffusion layer the catalyst bed which consists of a solid-state polyelectrolyte, carbon powder which supported the precious metal catalyst, and carbon powder which has a fluororesin 25 to 70% of the weight at least. The diameter of a primary particle is [the specific surface area of the carbon powder which supported said precious metal catalyst] 700-1000m2/g in 200-350A. The catalyst bed of the above-mentioned electrode offers the fuel cell using the electrode for polymer electrolyte fuel cells and it which are characterized by the structure where pore volume with a diameter of 0.04-1.0 micrometers is 0.04-0.13cm3/g.

[0012]

[Function] Since the solid-state polyelectrolyte 56 is not filled up with the pore 55 for gas channels formed between the catalyst support carbon particles 53 by the catalyst bed of the above pore structures as shown in <u>drawing 1</u> , gas supply ability can realize the electrode for polymer electrolyte fuel cells which demonstrates the highly excellent polarization property. By adding the carbon powder 60 furthermore given a water-repellent finish with the fluororesin 59 of <u>drawing 2</u> , the pore 55 for gas channels can be made to be able to increase, without covering the catalyst particle 52 with a fluororesin 59 too much, and water repellence can be raised, the polarization property in which gas supply ability and generation water discharge ability were highly excellent can be demonstrated, and the electrode for polymer electrolyte fuel cells which was excellent in electrical-potential-difference stability can be realized.

[0013]

[Example] Hereafter, an example explains this invention in more detail.

[0014] (Example 1) As an alcoholic solution of a solid-state polyelectrolyte, 5%Nafion solution by the Aldrich chemical company was mixed and stirred with 10ml of n-butyl acetate so that the amount of solid-state polyelectrolytes might serve as 0.1 - 1.4 mg/cm2, and the colloid dispersion liquid of a polyelectrolyte were generated. The carbon powder which made these colloid dispersion liquid support a platinum catalyst ten to 30% of the weight was added so that the amount of platinum might serve as 0.5 mg/cm2, and the solid-state polyelectrolyte was made to stick to the front face of the carbon powder which supported the catalyst. In addition, the diameter of a primary particle is [the specific surface area of this carbon powder] 700-1000m2/g in 200-350A. These dispersion liquid were made into the shape of a paste using the ultrasonic distribution machine. This paste was applied on the carbon paper by Toray Industries, Inc. which added 20 -

60% of the weight of the fluororesin beforehand, and the electrode A of this invention was produced. The hotpress of this electrode A was carried out to both sides of the Du Pont solid-state polyelectrolyte film Nafion117 by 120-200 degrees C and 5-100kg/cm2, and cell A' of this invention was produced.

[0015] (Example 2) To the colloid dispersion liquid of a solid-state polyelectrolyte, the carbon powder which added 25 to 70% of the weight, and gave PTFE a water-repellent finish further was added so that it might become 10 - 60 % of the weight to the carbon powder which supported the platinum catalyst, and also it presupposed that it is completely the same as that of (an example 1), and the electrode B of this invention and cell B' were produced.

[0016] (Example 1 of a comparison) It mixed with the carbon powder which made the platinum catalyst support ten to 25% of the weight, and the carbon powder which added 25 to 70% of the weight, and gave PTFE a water-repellent finish. The amount of platinum was made into 0.5 mg/cm2 at this time, and the water-repellent carbon powder was added so that it might become 40 % of the weight to the carbon powder which supported the platinum catalyst. This mixed powder for catalyst beds was sprinkled on the carbon paper which added the fluororesin 20 to 60% by the weight ratio, and carried out the hotpress by 340-360 degrees C and 5-20kg/cm2, and the electrode was produced. Addition of the solid-state polyelectrolyte to this electrode applied the solution which diluted 5%Nafion solution by the Aldrich chemical company with isopropyl alcohol so that the amount of solid-state polyelectrolytes might serve as 1.0 mg/cm2 in the condition of having drawn in with the pump from the carbon paper side, and used the approach of drying. Thus, the produced electrode C was joined to the solid-state polyelectrolyte film Nafion117 by the same approach as (an example 1), and cell C' was produced.

[0017] And pore distribution of said electrodes A, B, and C was measured with the method of mercury penetration using the mercury porosimeter (micro metrics company make, Auto Pore9220).

[0018] Moreover, the spark test was performed, having supplied the hydrogen and oxygen which were humidified at 60 degrees C to the forward negative electrode of cell A' of this invention, B', and comparative cell C', respectively, and having used cel temperature as 50 degrees C.

[0019] Change of pore volume with a diameter [when making the amount of solid-state polyelectrolytes into 0.1 - 1.4 mg/cm2 in Electrode A at drawing 3] of 0.04-1.0 micrometers is shown. Pore with a diameter of 0.04-1.0 micrometers functions as a gas channel with the hole formed in the floc of a carbon particle. In addition, by the diameter of a primary particle of carbon powder, those magnitude differs and this pore turns into a hole twice [more than] the diameter of the diameter of a primary particle. The solid-state polyelectrolyte entered into pore from the increment in the amount of solid-state polyelectrolytes, and pore volume decreased from 0.062cm3/g to 0.031cm3/g.

[0020] The relation between the pore volume of Electrode A, the current density 50,600 of cell A', and the cell voltage in 800 mA/cm2 was shown in drawing 4 . When pore volume was larger than 0.05cm3/g, the cell voltage in all current density became low. Moreover, when pore volume was smaller than 0.035cm3/g, the cell voltage in 600 and 800 mA/cm2 from which concentration polarization becomes dominant was low, and the stability of the electrical potential difference in a high current density region fell.

[0021] As shown in drawing 3 , at the case where pore volume is larger than 0.05cm3/g, there are few amounts of solid-state polyelectrolytes in a catalyst bed as less than two 0.5 mg/cm. From this, reaction area is small and it is thought that the cell voltage in 50 mA/cm2 which is the rule regions of activation polarization is low.

[0022] On the other hand, when pore volume is smaller than 0.035cm3/g, there are more amounts of solid-state polyelectrolytes in a catalyst bed than 1.2 mg/cm2. It is thought that the pore buried with a solid-state polyelectrolyte increased from this, gas supply ability fell, and the cell voltage in a high current density region fell. Furthermore, since there is much pore occupied with the solid-state polyelectrolyte of a hydrophilic property, generation water is held at an electrode catalyst bed, flooding becomes easy to happen, and it is thought that the stability of the cell voltage in a high current density region fell.

[0023] Thus, the polarization property that the cell using the electrode which has the catalyst bed whose pore volume is 0.035–0.05cm3/g is expensive, and the outstanding electrical-potential-difference stability were shown.
[0024] Subsequently, the volume of the pore of change of the volume of pore with a diameter [by the appending rate of the carbon powder with which Electrode B gave drawing 5 a water-repellent finish] of 0.04–1.0 micrometers, and the comparative electrode C was shown. In addition, the amount of solid-state polyelectrolytes at this time was made into 1.0 mg/cm2. The pore volume of the electrode B of this invention increased by the increment in the appending rate of the water-repellent carbon powder, and the appending rate of the carbon powder given especially a water-repellent finish increased remarkably at 30 % of the weight or more. On the other hand, the water-repellent carbon powder of the pore volume of Electrode C was as large as 0.164cm3/g as compared with 0.090cm3/g of the electrode B of this invention which is tales doses.
[0025] The thickness of the catalyst bed in each appending rate of the carbon powder which gave (Table 1) a water-repellent finish was shown.
[0026]
[Table 1]

撥水処理炭素粉末の添加率／重量%	0	10	20	30	40	50	60
触媒層厚み／μm	8	22	25	32	45	51	65

[0027] The increment in water-repellent-finish carbon powder shows that the thickness of a catalyst bed is large.
[0028] Relation with the cell voltage in the current density 50,600 and 1000 mA/cm2 of the pore volume of the electrode C of the comparison of the electrode B of this invention with drawing 6 , cell B', and C' was shown. The electrical potential differences of cell B' of this invention were 780–830mV and a high value to the electrical potential difference of comparative cell C' being 750mV. Moreover, in cell B', the electrical potential difference in 50 mA/cm2 which is the rule regions of activation polarization fell slightly by the increment in pore volume. By 600 and 1000 mA/cm2 which are the rule regions of concentration polarization, cell B' showed high cell voltage to cell C'. Moreover, cell voltage rose with the increment in pore volume, and the stability of cell voltage also improved. However, cell voltage lower than what does not add the carbon powder given a water-repellent finish when pore volume became larger than 0.130cm3/g was shown, and the stability of cell voltage worsened.
[0029] The sag in a low current consistency region came out only, and became possible [controlling reduction of covering of the platinum catalyst by PTFE, i.e., the reaction area of a catalyst, by addition of the water-repellent carbon powder] from a certain thing. Although the thickness of an electrode increases by addition of the carbon powder furthermore given a water-repellent finish, as shown in drawing 5 , the pore which is a gas channel increases, the gas supply ability to a reaction site improves, and the electrical potential difference in a high current density region can be referred to as going up. Since a gas channel is furthermore formed by water-repellent PTFE, it is thought that discharge of generation water is performed more smoothly and the stability of cell voltage improves. However, a gas channel becomes larger than 0.130cm3/g, namely, if water-repellent-finish carbon powder becomes superfluous, it will be thought that the effectiveness of gas channel formation is negated by covering of a platinum catalyst and the increment in electrode thickness by PTFE, and the stability of cell voltage and cell voltage falls.
[0030] Thus, when the carbon powder which gave a water-repellent finish by adding a fluororesin was added, the cell using the electrode whose pore volume is 0.040–0.130cm3/g showed the high property.
[0031] in addition, drawing 5 and drawing 6 -- and (Table 1) -- **** -- although the amount of solid-state polyelectrolytes was made into 1.0 mg/cm2, the property that the amount of solid-state polyelectrolytes is equivalent in the pore volume range same in 0.6 – 1.2 mg/cm2 was acquired.
[0032] Moreover, although n-butyl acetate was used as an organic solvent, if it is the solvent

which produces the colloid dispersion liquid of a solid-state polyelectrolyte, it will not be limited to this. Moreover, although it is desirable to choose the amount which more detailed colloid dispersion liquid generate as for the addition of the above-mentioned organic solvent, the example of this invention indicates the central value, and does not limit an effect of the invention.
[0033] moreover, the thing which will be limited to the above-mentioned example if it is a polyelectrolyte with a proton exchange group although 5%Nafion solution by U.S. Aldrich Chemical was used as a solid-state polyelectrolyte in the example as an example of representation of the giant molecule which consists of a copolymer of tetrafluoroethylene and perfluoro vinyl ether — it is not — the molecular structure — things — the same effectiveness was acquired in the giant molecule. For example, the giant molecule with which perfluoro vinyl ether differs from side-chain molecule length, and the giant molecule which consists of a copolymer of styrene and vinylbenzene may be used.
[0034] Although the hydrogen-oxygen fuel cell was furthermore taken up as an example of a fuel cell by this example, it is also possible to apply a methanol, natural gas, naphtha, etc. to the fuel cell using the reforming hydrogen used as a fuel or the fuel cell using air as an oxidizer, and the liquid fuel cell that used the methanol for the fuel directly.
[0035]
[Effect of the Invention] Since the pore formed between carbon particles as a gas channel is not filled up with a solid-state polyelectrolyte in an electrode catalyst bed as mentioned above according to this invention, gas supply ability can realize the electrode for polymer electrolyte fuel cells which demonstrates a high more high polarization property. By adding the carbon powder furthermore given a water-repellent finish with the fluororesin, the increment and the water-repellent improvement in a gas channel can be performed without covering a catalyst particle with a fluororesin too much, gas supply ability and generation water discharge ability can demonstrate a high more high polarization property, and the electrode for polymer electrolyte fuel cells which was excellent in electrical-potential-difference stability can be realized.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The schematic diagram showing the cross section of the electrode of this invention
[Drawing 2] The schematic diagram showing the cross section of other electrodes of this invention

[Drawing 3] Drawing showing the relation between pore volume and a solid-state polyelectrolyte addition
[Drawing 4] Drawing showing the relation between the electrical potential difference of a fuel cell, and pore volume
[Drawing 5] Drawing showing the relation between pore volume and water-repellent-finish carbon powder
[Drawing 6] Drawing showing relation with the electrical-potential-difference-pore volume of a fuel cell
[Description of Notations]
11 Solid-state Polyelectrolyte Film
51 Catalyst Bed
52 Catalyst Particle
53 Catalyst Support Carbon Powder
55 Pore
56 Solid-state Polyelectrolyte
57 Gaseous Diffusion Layer
58 Solid-state Polyelectrolyte Film
59 Fluororesin
60 Water-repellent-Finish Carbon Powder

[Translation done.]